

PATENT SPECIFICATION

NO DRAWINGS

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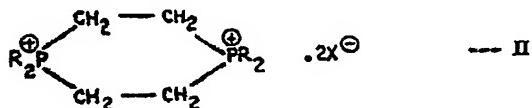
COMPLETE SPECIFICATION

Polymeric Quaternary Phosphorus Compounds and method of preparing same

We, AMERICAN CYANAMID COMPANY, a corporation organised under the laws of the State of Maine, United States of America, of 30 Rockefeller Plaza, New York, State of 5 New York, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the 10 following statement:—

The present invention relates to quaternary phosphorous compounds and to the method of preparing same. More particularly, the instant discovery concerns the preparation of 15 1,4-diphosphoniacyclohexanes from secondary phosphines.

The present invention is concerned with substituted dimeric or polymeric phosphonium salts having the following structural 20 configuration in the molecule



wherin R and X are as defined above.

In accordance with the present invention 35 there is provided a process for preparing substituted dimeric or polymeric phosphonium salts having the structural configuration I and II above characterized by,

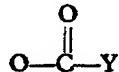
(a) reacting a secondary phosphine of the 40 general formula



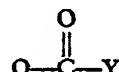
with a vinyl derivative of the general formula



wherin R is as defined above and X is a 45 Cl, Br or I atom or an



radical, wherin Y is a lower-alkyl group of 1 to 6 carbon atoms, in the presence of a free radical initiator which is non-oxidizing to the 50 reactants, and then, if desired, when R bears a nitrile substituent hydrolyzing the nitrite to form a carboxyl substituent and/or when X is

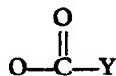


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treating with an iodide or bromide to convert the corresponding compound to the diiodide or dibromide,



wherein R is a substituted or unsubstituted branched or straight chain alkyl radical or a substituted or unsubstituted cycloalkyl radical, and X is a chlorine, bromine, or 25 iodine atom or a sulfate, phosphate or



radical, wherein Y is a lower-alkyl group of 1 to 6 carbon atoms; and wherein n is an integer of at least 2 and when n is 2 the phosphonium salt is a cyclic structure of the following configuration

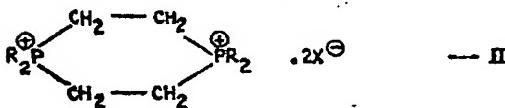
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(b) and, if desired, heating the polymer to convert it into the dimer

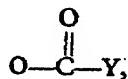
(c) and also, if desired, subjecting the dimer or the polymer to an anionic exchange treatment to convert X to sulfate or phosphate.

Also in accordance with this invention there is provided a process as described above in which the polymer produced has an average molecular weight of between 5,000 and 10,000. Another feature of this invention is that the temperature of the condensation of the compounds of formula III with those of the formula IV is preferably from 70° C. to 140° C. Still another feature of this invention is the conversion of the straight chain polymer to the cyclic dimer (II) by heating, preferably at a temperature of at least 160° C. Still another feature of this invention is the use of some polymeric phosphonium salts of formula I in the condensation of the compounds of formula III with compounds of formula IV as promoters of the reaction.

According to the present discovery a cyclic quaternary phosphorus compound is produced corresponding to the formula



wherein R is a substituted or unsubstituted, branched or straight chain alkyl radical, a substituted or unsubstituted cycloalkyl radical and X is a radical selected from the group consisting of Br, Cl, I, and



Y being a lower alkyl radical containing 1 to 6 carbon atoms, by bringing a secondary phosphine conforming to the formula



R in this formula corresponding to R in the product formula, above, into reactive contact with a member selected from the group consisting of vinyl chloride, vinyl bromide, vinyl iodide, and a vinyl carboxylate, including vinyl acetate, vinyl propionate and vinyl butyrate, and recovering the corresponding 1,4-di-phosphonacyclohexane salt.

Reaction is made to take place in the presence of a non-oxidizing free radical initiator, such as di-t-butylperoxide, 2,2'-azobisisobutyronitrile, ultraviolet light or X-ray radiation. In addition, and if desired, a

solvent may be employed, such as acetonitrile, heptane, dioxane or methyl ethyl ketone, which solvent is substantially inert under the conditions of reaction with respect to the reactants, the reaction mixture, and the product.

Among the many secondary phosphines suitable for use in the present invention are bis(2 - cyanoethyl)phosphine, bis(2 - carboxyethyl)phosphine, bis(2 - butoxyethyl)phosphine, dimethylphosphine, dibutylphosphine, diisobutylphosphine, didodecylphosphine, dicyclohexylphosphine, bis(2 - methoxyethyl)phosphine and bis(2 - carbomethoxyethyl)phosphine.

Included among the substituents contemplated for the dialkyl- and dicycloalkyl-moieties of the secondary phosphines are carboxy-, cyano-, sulfonic and amido groups.

Although the use of a very substantial excess of either reactant is contemplated herein, a preferred ratio of reactants is in the range of equimolar proportions up to about 10 moles of the secondary phosphine per mole of vinyl acetate or vinyl bromide.

Temperatures in the range of 30° C. to 200° C., preferably 70° C.—140° C., are best suited for carrying out the process of the present invention. Of course, when the reaction is made to take place in the presence of an inert solvent a desirable temperature upper limit is generally that at which the solvent boils.

According to a preferred embodiment of the instant invention, the reactants are brought together at a temperature in the range of 70° C. to 140° C. and in the presence of a non-oxidizing free radical initiator. The temperature is maintained at above 50° C., preferably above 70° C., and below 140° C. throughout the reaction, i.e., until the reaction ceases. Typically, these temperatures are maintained by alternate cooling and heating until cessation of temperature fluctuations which are particularly noticeable, for example, in the case of vinyl acetate. With the vinyl halides, on the other hand, the fluctuations are not quite as evident.

When admixing vinyl acetate and a secondary phosphine, for example, in the presence of a non-oxidizing free radical initiator and at a temperature in the range of 70° C.—140° C., a spontaneous rise in temperature followed by an equally spontaneous temperature drop is usually observed. By cooling and heating, as required, temperatures in the desired range may be maintained. Depending upon the reactivity of the reactants, reaction is complete when the fluctuations terminate and a substantially constant temperature is observed for a reasonable period of time.

It is noted that the temperature at which the reactants are admixed, the individual reactivity of these reactants, the total amount and ratio of reactants used, as well as the

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degree of admixing provided, are all factors in determining optimum reaction times. Generally, assuming satisfactory admixing and the use of equimolar amounts of each reactant, reaction times at temperatures from 70° C.—140° C. are from at least about 5 minutes to about 120 minutes or more. However, substantially longer periods of time up to 3 to 5 hours or more may be employed, if desired.

Usually, though, if the total quantity of reactants is not too large, up to 3 hours is sufficient.

The instant process may be continuous, semi-continuous or batch. Furthermore, suitable results are obtained by operating at atmospheric, sub-atmospheric or super-atmospheric pressures.

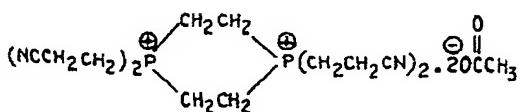
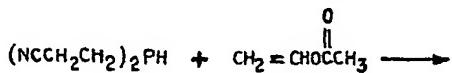
It should be noted that when using vinyl bromide, vinyl chloride, dimethylphosphine, or other similar volatile reactants, the reaction is best carried out at super-atmospheric pressures, particularly if temperatures above about 70° C. are employed. This, of course, is to prevent loss of reactants caused by volatilization.

Generally, with these and like reactants, pressures in the range of 1 atmosphere to 30 atmospheres are suitable. However, substantially higher pressures are also contemplated herein.

The cyclic dimer products produced herein are advantageously applied to wool, for example, to give lasting protection against injurious insects, such as moths, and the like. The polymer products herein are particularly useful as non-durable antistatic agents for use in textile finishes.

The present invention will best be understood by reference to the following examples which are intended to be illustrative and not unduly limiting to the scope of the invention; for, as will be seen hereinafter, the instant discovery admits of numerous modifications within the scope of the appended claims:

EXAMPLE I.
1,1,4,4 - tetrakis(2 - cyanoethyl) - 1,4 - di-phosphoniacyclohexane diacetate



A solution of 18.9 grams (0.22 mole) of vinyl acetate and 1.5 grams (0.01 mole) of 2,2'-azodiisobutyronitrile in 20 milliliters of acetonitrile is added dropwise and continuously over a period of 20 minutes and with stirring to 28.0 grams (0.20 mole) of bis(2-cyanoethyl)phosphine which has been warmed to 76° C. under an atmosphere of nitrogen. The reaction temperature is held at 78° C.—95° C. during admixing of reactants and subsequently by intermittent cooling in a water bath and heating when required. After a total time of 45 minutes (including 20 minutes addition time), the resulting opaque, tan, viscous mixture is cooled to room temperature (21° C.—23° C.) and stirred into 250 milliliters of acetone. Much of the reaction mixture dissolves, leaving 22.5 grams (50 per cent by weight of theory) of a white crystalline solid having a melting point of 150° C.—151° C.

A portion of this product material is dissolved in boiling isopropyl alcohol containing a few drops of water, and the resulting solution is diluted with 2 volumes of acetone. After standing several days at —10° C. crystals obtain from this solution, which crystals of 1,1,4,4 - tetrakis(2-cyanoethyl) - 1,4 - diposphoniacyclohexane diacetate, after drying at 53° C. over P₂O₅, melt at 149° C.—150° C.

Analysis calculated for C₂₀H₃₀N₄O₄P₂: P, 13.69.
Found: P, 13.60, 13.96.

A portion (2 grams) of this product phosphonium acetate is dissolved in 100 milliliters of water and treated with a saturated aqueous sodium bromide solution. The corresponding phosphonium bromide precipitates and is

twice recrystallized from water to obtain 1.9 grams of long needles of 1,1,4,4-tetrakis(2-cyanoethyl) - 1,4 - diposphoniacyclohexane dibromide having a melting point of 303° C.—304° C.

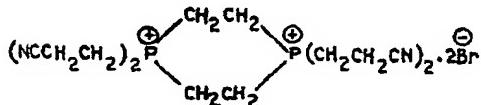
Analysis calculated for C₁₆H₂₄Br₂N₄P₂: Br, 32.34; P, 12.53.
Found: Br, 32.81; P, 12.94.

Another small portion of the phosphonium acetate product, above, is dissolved in water and treated with a saturated aqueous potassium iodide solution. The resulting insoluble iodide is recrystallized from water to obtain

an analytical sample of 1,1,4,4 - tetrakis(2-cyanoethyl) - 1,4 - diposphoniacyclohexane diiodide having a melting point of about 320° C.

Analysis calculated for $C_{16}H_{24}I_2N_4P_2$: I, 43.15; P, 10.53.
Found: I, 43.19; P, 10.60.

EXAMPLE II.
Reaction of bis(2-cyanoethyl)phosphine with
5 Vinyl Bromide

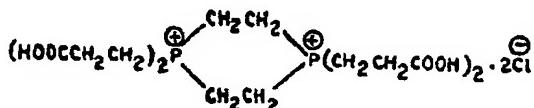
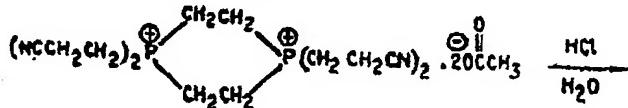


A slow stream of vinyl bromide is passed

continuously during a 30-minute period into a stirred solution of 12.5 grams of bis(2-cyanoethyl)phosphine and 0.80 gram of 2,2'-azodiisobutyronitrile in 35 milliliters of acetonitrile heated at 80° C. An oil begins to separate almost immediately. Upon cooling the oil congeals to a white gum which is separated and extracted with hot water. The extract, when cool, deposits 1.8 grams of crystalline solid having a melting point of 300° C.—303° C. A mixed melting point with the bromide salt obtained in Example I, above, is not depressed. Furthermore, the infrared spectra of the two products are identical.

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EXAMPLE III.
1,1,4,4 - tetrakis(2 - carboxyethyl) - 1,4 -
diphosphoniacyclohexane dichloride



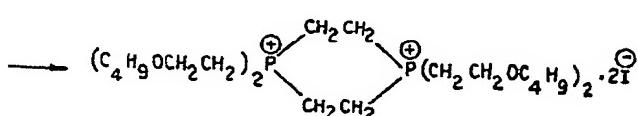
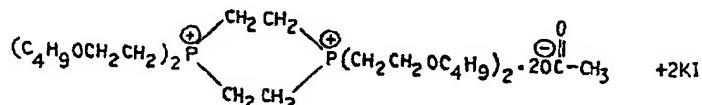
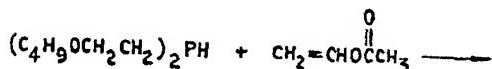
Five grams (0.011 mole) of 1,1,4,4-tetrakis(2 - cyanoethyl) - 1,4 - diphosphoniacyclohexane diacetate produced as in Example I, above, is dissolved in 10 milliliters of warm concentrated HCl. After refluxing 5 minutes the solution congeals to a white mass. An additional 20 cubic centimeters of concentrated HCl is added and the mixture refluxed for 1 hour.

After cooling to room temperature, the

resulting solid is filtered and washed with acetone, yielding 5.5 grams of material having a melting point of 259° C.—260° C. Recrystallization of this material from about 6 per cent aqueous HCl, followed by recrystallization from aqueous acetone produces 3.7 grams (70 per cent by weight of theory) of 1,1,4,4 - tetrakis(2 - carboxyethyl) - 1,4 - diphosphoniacyclohexane dichloride having a melting point of 280° C.—282° C.

Analysis calculated for $C_{16}H_{24}Cl_2O_8P_2$: C, 39.93; H, 5.86; P, 12.87; Cl, 14.73.
Found: C, 39.83; H, 6.05; P, 12.85; Cl, 14.72.

EXAMPLE IV.



- 5 A solution of 12.2 grams (0.05 mole) of bis(2-butoxyethyl phosphine, 4.5 grams (0.05 mole) of vinyl acetate, 0.5 gram (0.003 mole) of 2,2¹-azodiisobutyronitrile and 10 milliliters of acetonitrile is warmed at 78° C.—84° C.
10 for 30 minutes. A vigorous reaction occurs and the reaction mixture becomes dark brown. The resulting weakly basic solution is combined with 100 milliliters of acetone and made acidic (pH 4) with concentrated hydrochloric acid. No precipitation takes place but the color changes from brown to light yellow. A saturated aqueous potassium iodide solution is then added until precipitation is complete. The precipitate (potassium chloride, 4.1 grams) is removed by filtration and the filtrate concentrated to 10 milliliters
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under vacuum. The concentrate consists of a gummy solid and a supernatant liquid consisting of water and acetic acid. This solid is treated with a mixture of 50 milliliters of acetone and 50 milliliters of ether. A crystalline solid results which is collected by filtration to obtain 3.7 grams of 1,1,4,4-tetrakis(2-butoxyethyl) - 1,4 - diphosphoniacyclohexane diiodide product having a melting point of about 261° C. The iodide is recrystallized once from 50 per cent aqueous ethanol and again from 75 per cent ethanol to obtain 2.0 grams of pale yellow needles of 1,1,4,4-tetrakis(2 - butoxyethyl) - 1,4 - diphosphoniacyclohexane diiodide having a melting point of 271° C.—273° C.

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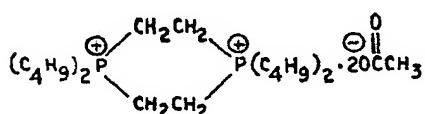
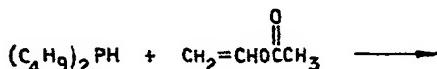
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Analysis calculated for $C_{28}H_{46}I_2O_4P_2$: P, 7.97.
Found: P, 7.96.

EXAMPLE V

1,1,4,4 - tetrabutyl - 1,4 - diphosphoniacyclohexane diacetate



- A solution of 73.4 grams (0.5 mole) of di-*n*-butylphosphine, 2.0 grams (0.012 mole) of 2,2¹ -azodiisobutyronitrile, and 100 milliliters of heptane is warmed to 78° C. under an atmosphere of nitrogen, and 43.2 grams (0.5 mole) of vinyl acetate is added dropwise

and continuously with stirring during a 15-minute period. The temperature of the mixture is maintained at 78° C.—83° C. during addition by means of intermittent cooling. The resulting reaction mixture is then stirred at 80° C.—85° C. for 1 hour and at 95° C. for 15 minutes. The solvent in the reaction mixture is then removed by distillation under reduced pressure, thus leaving a liquid residue which is heated to 95° C. for 30 minutes and which congeals to a dark brown tarry mass. Next, three hundred milliliters of ether is added to the mixture and the mixture stirred and refluxed for 1 hour. The tarry material dissolves leaving 69.0 grams of a white crystalline solid. A portion of the solid is recrystallized from benzene containing a small amount of ethanol to obtain an analytical sample of 1,1,4,4 - tetrabutyl - 1,4 - diphosphoniacyclohexane diacetate product having a melting point of 195° C.

Analysis calculated for $C_{24}H_{30}O_4P_2$: P, 13.33.
Found: P, 13.65.

This acetate product is highly soluble in water or ethanol but is insoluble in hot acetone or ethyl acetate. 5 until precipitation is complete. The resulting white product is twice recrystallized from butanol to obtain an analytical sample of the corresponding 1,1,4,4 - tetrabutyl - 1,4 - diphosphoniacyclohexane dibromide having a melting point of 316° C.—319° C. 10

Ten grams of the product is dissolved in 50 milliliters of water and treated with a saturated aqueous sodium bromide solution

15 Analysis calculated for $C_{29}H_{44}Br_2P_2$: P, 12.23.
Found: P, 12.20.

This bromide is soluble in water and absolute ethanol and insoluble in acetone.

20 Another ten-gram portion of the acetate product is dissolved in 50 milliliters of water and treated with a saturated aqueous potassium iodide solution until precipitation is

complete. The resulting white solid is recrystallized from 500 milliliters of water to obtain 7.8 grams of 1,1,4,4-tetrabutyl-1,4-diphosphoniacyclohexane diiodide having a melting point of 340—342° C. 25

Analysis calculated for $C_{26}H_{44}I_2P_2$: I, 43.58.
Found: 43.31, 43.71.

30 EXAMPLE VI.
1,1,4,4 - tetradodecyl - 1,4 - diphosphoniacyclohexane diacetate

A mixture of 7.0 grams (0.02 mole) of didodecylphosphine, 4.8 grams (0.06 mole) of vinyl acetate, 0.5 gram of 2,2'-azodiisobutyronitrile, and 10 milliliters of acetonitrile is heated at 80° C.—85° C. under an atmosphere of nitrogen for 2 hours. The infrared spectrum of the reaction mixture indicated

the presence of acetate ion. The addition of 40 50 milliliters of acetone precipitates 2.4 grams (28 per cent by weight of theory) of yellow solid having a melting point of 132° C.—135° C. Three recrystallizations from a mixture of ethyl acetate and isopropyl alcohol provide a pure sample of 1,1,4,4-tetradodecyl-1,4 - diphosphoniacyclohexane diacetate having a melting point of 144° C.—147° C. 45

50 Analysis calculated for $C_{36}H_{64}O_4P_2$: C, 73.63; H, 12.58; P, 6.78.
Found: C, 70.14; H, 11.67; P, 6.56.

EXAMPLE VII

1,1,4,4 - tetracyclohexyl - 1,4 - diphosphoniacyclohexane diiodide

55 A mixture of 9.9 grams (0.05 mole) of dicyclohexylphosphine, 4.3 grams (0.05 mole) of vinyl acetate, 0.5 gram of 2,2'-azodiisobutyronitrile, and 10 milliliters of acetonitrile is heated at 80° C.—85° C. under an atmosphere of nitrogen for 2 hours. The solvent 60 is evaporated under reduced pressure. The solvent is boiled off under an atmosphere of nitrogen until the temperature reaches 150° C. An amber liquid results which is cooled to room temperature (21° C.—23° C.). To induce crystallization a 50-milliliter quantity

of ether is added and the white solid (2.1 grams) thus formed is filtered and washed with ether; it has a melting point of 80° C.—95° C. An excess of a saturated aqueous potassium iodide solution is added to an aqueous solution of a portion of this product solid. The resulting white solid is filtered off and washed with water; it has a melting point of 315° C. Purification is effected by boiling the product solid in dimethylformamide, recovering it by filtration, and washing it with acetone. The product thus purified is 1,1,4,4-tetracyclohexyl - 1,4 - diphosphoniacyclohexane diiodide having a melting point of 317° C. 70 75 80

Analysis calculated for $C_{28}H_{52}I_2P_2$: C, 47.74; H, 7.44; P, 8.79.
Found: C, 47.62; H, 7.41; P, 8.50.

EXAMPLE VIII

1,1,4,4 - tetraisobutyl - 1,4 - diphosphonia-
cyclohexane diiodide

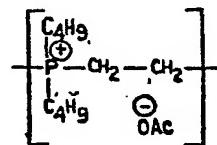
A solution of 18.0 grams (0.12 mole) of 5 diisobutylphosphine, 10.6 grams (0.12 mole) of vinyl acetate, and 1.0 gram of tertiary-butyl peroxide in 20 milliliters of acetonitrile is placed in a 100-milliliter stainless steel pressure vessel and heated at 125° C.—135° 10 C. for 10 hours. The resulting dark brown, viscous reaction product is treated with 75 milliliters of water, and the mixture is extracted with ether. The extract is discarded and the aqueous solution treated with an 15 excess of saturated sodium iodide solution. An insoluble tan solid separates and is collected. It is washed three times with 25-milliliter portions of hot acetone and recrystallized from dimethylformamide to 20 obtain relatively pure phosphonium iodide.

EXAMPLE IX

1,1,4,4 - tetraisobutyl - 1,4 - diphosphonia-
cyclohexane diiodide

A solution of 9.0 grams (0.06 mole) of 25 diisobutylphosphine, 5.3 grams (0.06 mole) of vinyl acetate and 10 milliliters of acetonitrile is placed in a clear quartz tube and irradiated with ultraviolet light for 2 hours at 30° C. The reaction mixture is transferred 30 to a flask and the solvent boiled off until the temperature reaches 130° C. The resulting dark brown, viscous mixture is treated with 30 milliliters of water, and the mixture extracted with ether. The extract is discarded, 35 and the aqueous solution treated with an excess of saturated sodium iodide solution. A tan solid separates and is recrystallized from dimethylformamide to obtain the product.

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EXAMPLE X
Preparation of Polymeric Dibutyl Phosphonium AcetateEXAMPLE X
Preparation of Polymeric Dibutyl Phosphonium Acetate

The process of Example V is repeated through the step involving the addition of vinyl acetate at 78° C.—83° C. over a 15 minute period except that isopropanol is used as the solvent instead of heptane. Following said step the reaction mixture is heated at 80° C. for 16 hours, whereupon 300 ml. of ethyl acetate is added and the reaction mixture is cooled to room temperature and filtered. The filter cake is dried in vacuo and thereby 50 grams of polymeric dibutyl phosphonium acetate of MP 151—5° C. are obtained. The polymeric nature of the acetate is confirmed by measuring the intrinsic viscosity of the corresponding bromide salt, the latter being obtained by treating a 25% aqueous solution of the acetate salt with aqueous saturated sodium bromide solution and filtering off the precipitated bromide salt.

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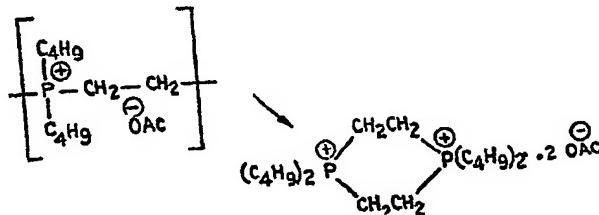
EXAMPLE XI

Preparation of Polymeric Dibutyl Phosphonium Acetate

The process of Example X is repeated except that (1) 0.5 gram of polymeric dibutyl phosphonium acetate prepared as in Example X is added to the reaction mixture after the addition of vinyl acetate is complete and (2) the reaction time is 4 hours instead of 16 hours. The final polymer has a MP of 151—4° C.

EXAMPLE XII

Preparation of 1,1,4,4 - Tetrabutyldiphosphonia Cyclohexane Diiodide



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Three grams of a polymeric dibutyl phosphonium acetate as prepared in Example XI is heated under nitrogen at 160—165° C. for 20 minutes. The solid gradually melts to a red oil. The oil is cooled to room tempera-

ture and shaken with a mixture of 75 ml. of benzene and 25 ml. of water. The benzene phase is separated and washed twice with 25 ml. portions of water. The aqueous solutions are combined, diluted to 150 ml. with water

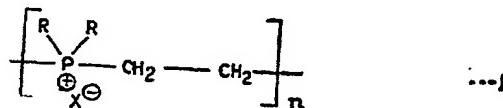
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and treated with aqueous potassium iodide solution until precipitation is complete. The mixture is filtered to obtain 1.4 gram of white solid. The solid is stirred with 75 ml. of acetone and filtered to obtain 1.2 gram of the cyclic diphosphonium diiodide, MP 337-8° C. (with decomposition). A mixed melting point with an authentic sample as prepared in Example V was not depressed.

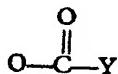
While the present invention has been described in detail as to specific embodiments thereof, it is not intended that these details exert undue restrictions upon the scope of the invention, except insofar as they appear in the appended claims.

WHAT WE CLAIM IS:-

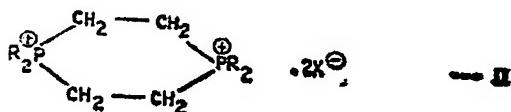
1. A process for preparing substituted dimeric or polymeric phosphonium salts having the following structural configuration in the molecule



wherein R is a substituted or unsubstituted branched or straight chain alkyl radical or a substituted or unsubstituted cycloalkyl radical, and X is a chlorine, bromine, or iodine atom or a sulfate, phosphate or

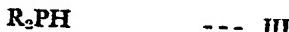


radical, wherein Y is a lower-alkyl group of 1 to 6 carbon atoms; and wherein n is an integer of at least 2 and when n is 2 the phosphonium salt is a cyclic structure of the following configuration



wherein R and X are as defined above characterized by,

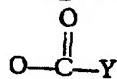
(a) reacting a secondary phosphine of the general formula



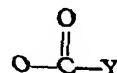
with a vinyl derivative of the general formula



wherein R is as defined above and X is a Cl, Br or I atom or an



radical, wherein Y is a lower-alkyl group of 1 to 6 carbon atoms, in the presence of a free radical initiator which is non-oxidizing to the reactants, and then, if desired, when R bears a nitrile substituent hydrolyzing the nitrile to form a carboxyl substituent and/or when X is



treating with an iodide or bromide salt to convert the corresponding compound to the diiodide or dibromide

(b) and, if desired, heating the polymer to convert it into the dimer

(c) and also, if desired, subjecting the dimer or the polymer to an anionic exchange treatment to convert X to sulfate or phosphate.

2. A process according to claim 1 characterized by the fact that n has a value so that the polymer has an average molecular weight of between 5,000 and 10,000.

3. A process according to claim 1 or 2 characterized by the fact that the free radical initiator is di-t-butyl peroxide, 2,2'-azobisisbutyronitrile, ultraviolet light or X-ray irradiation.

4. A process according to any one of the preceding claims characterized by the fact that a solvent is also present during the reaction.

5. A process according to any one of the preceding claims characterized by the fact that the temperature of the reaction in step (a) is from 70° C. to 140° C.

6. A process according to any one of the preceding claims characterized by the fact that some polymeric phosphonium salt of formula I is present during the reaction in step (a) as a promoter.

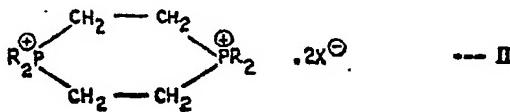
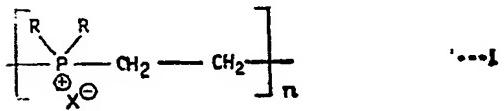
7. A process according to any one of the preceding claims characterized by the fact that the temperature of the conversion of polymer to dimer in step (b) is at least 160° C.

8. A process according to any one of the preceding claims characterized by the fact that R is one of the following: 2-cyanoethyl, 2-carboxyethyl, 2-butoxyethyl, n-butyl, or cyclohexyl.

9. A process for preparing substituted dimeric or polymeric phosphonium salts as defined in claim 1 substantially as described.

10. Substituted dimeric or polymeric phosphonium salts whenever prepared by the process substantially as described.

11. Substituted dimeric or polymeric phosphonium salts having the following structural configuration in the molecule integer of at least 2 and wherein n is 2 the phosphonium salt is a cyclic structure of the following configuration 15



- 5 wherein R is a substituted or unsubstituted branched or straight chain alkyl radical or a substituted or unsubstituted cycloalkyl radical, and X is a chlorine, bromine, or iodine atom or a sulfate, phosphate or



radical, wherein Y is a lower-alkyl group of 1 to 6 carbon atoms; and wherein n is an

wherein R and X are as defined above.

12. Salts according to claim 11 wherein R is one of the following: 2 - cyanoethyl, 2 - carboxyethyl, 2 - butoxyethyl, n - butyl, or cyclohexyl. 20

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